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Short communication

Li_2FeSiO_4/C cathode material synthesized by template-assisted sol–gel process with Fe_2O_3 microsphere

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HIGHLIGHTS

- Li_2FeSiO_4/C nanocomposite is prepared by sol–gel method with Fe_2O_3 microsphere.
- It exhibits sphere-like morphology.
- It owns stable cycle performance at 0.1 C–2 C rate.

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ABSTRACT

Fe_2O_3 microsphere is used as iron source and template to prepare Li_2FeSiO_4/C nanocomposite by a sol–gel method. The carbon content, structure, and morphology of the sample are characterized by carbon–sulfur inferred analysis (CSI), X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscopy (TEM) techniques. The results show that the Li_2FeSiO_4/C owns pure phase and sphere-like morphology as a result of an agglomeration of nanoparticles with an average particle size of about 50 nm. The Li_2FeSiO_4/C exhibits stable cycle performance at different rates from 0.1 C to 2 C, and its capacity at 0.1 C rate can reach 160 mAh g^{-1}.

1. Introduction

Lithium-ion batteries have been widely applied on the portable electric power tools and other electronic products, and they are considered as the promising power sources of electric vehicles (EVs) [1]. During the past decade, polyanion-type compounds containing $(XO_4)^{n-}$ group as the cathode materials of lithium-ion batteries have attracted much attention because of their low exothermicity and high safety, compared with lithium transition-metal oxides, such as $LiMn_2O_4$, $LiCoO_2$, and $Li[Ni,Co,Mn]O_2$ [2,3]. Among the polyanion compounds, lithium transition-metal orthosilicate (Li_2MSiO_4, M = Fe, Mn, *etc.*) own the higher theoretical capacity (2 mol of Li^+ per formula unit) [4–8]. Recently, more and more researchers focus on Li_2FeSiO_4, due to its excellent cycle performance [9–25]. In addition, Li_2FeSiO_4 is inexpensive, nonpoisonous, and environmental friendly, because the elements of O, Si, and Fe are contained most abundantly on the earth.

However, Li_2FeSiO_4 suffers from the problem of poor electronic conductivity and slow diffusion rate of lithium ion [10,26], which prevent it from further applications. It is reported that preparing carbon-coated Li_2FeSiO_4 composite (Li_2FeSiO_4/C) and decreasing particle size to nano-scale are two effective approaches to overcome these obstacles [27,28]. Up to now, great efforts have been offered to prepare Li_2FeSiO_4/C as the cathode material for lithium-ion battery by different synthetic methods [6,7,9–25]. Solid-state reaction method is appropriate to the large-scale production, but the impurities and the larger particle size of the product could not be avoidable, due to the prolonged heat treatment at a high temperature [6,20,22,23]. Direct hydrothermal method is difficult to acquire Li_2FeSiO_4 or Li_2FeSiO_4/C with pure phase, and the products own low crystallinity, which make negative effects on the electrochemical performances of the products, although this approach can reduce the particle size [7,9,25]. Sol–gel method can greatly improve the homogeneity of the precursor, and the as-

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prepared Li_2FeSiO_4/C exhibits pure phase, nano-scale particle size, and excellent electrochemical performance. For example, Dominko et al. have firstly synthesized Li_2FeSiO_4/C composite basing on sol–gel reflux method, by using the soluble $Fe(NO_3)_3$, or $FeC_6H_5O_7$ (ferric citrate) as Fe source and the insoluble nano-SiO_2 as Si source [9]. If the nano-SiO_2 is replaced by the soluble silicane, such as tetraethyl orthosilicate (TEOS), the molecular-level mixing of Li, Fe and Si elements can be achieved during the process of forming sol–gel. Representatively, the Li_2FeSiO_4/C nanocomposites have been prepared by the microwave-solvothermal and hydrothermal-assisted sol–gel methods, and the products show better performance [11,14]. Furthermore, the *in-situ* generated carbon can help to restrict the increasing of the Li_2FeSiO_4 particle size during the heat treatment. Through modifying the carbon coating techniques, the electrochemical properties of Li_2FeSiO_4 could also be improved. Recently, porous Li_2FeSiO_4/C have been prepared by introducing carbon source during sol–gel process, and more than 1 mol of Li^+ per formula unit can be extracted from the porous Li_2FeSiO_4/C [16,17].

Usually, the main impurities in the Li_2FeSiO_4/C are iron oxides and lithium silicates in the previous investigations, which are looked on as the infaust factors to electrochemical performance [7,20]. Is it possible to replace iron salts by iron oxides to prepare pure-phased Li_2FeSiO_4/C *via* simple processes? This assumption had been proved to be feasible in this work. Fe_2O_3 microsphere is used as the Fe source and template to synthesize the sphere-like Li_2FeSiO_4/C nanocomposite by sol–gel method. Furthermore, the Li_2FeSiO_4/C nanocomposite exhibits stable cycle performance at different rates from 0.1 C to 2 C.

2. Experimental

2.1. Preparation of Fe_2O_3 microsphere

All the reagents and solvents were analytical purity, and purchased from Sinopharm Chemical Reagent Co. Ltd., and used as received. Fe_3O_4 microsphere was synthesized by hydrothermal method as described in the literature [29]. In order to remove the absorbed surfactants, Fe_3O_4 microsphere was heated at 400 °C for 2 h under atmosphere to obtain Fe_2O_3 microsphere.

2.2. Preparation of Li_2FeSiO_4/C composites

The Li_2FeSiO_4/C composite was synthesized by sol–gel method. Typically, the stoichiometric amounts of $LiCH_3COO{\cdot}2H_2O$ (0.02 mol), as-prepared Fe_2O_3 microsphere (0.005 mol), and TEOS (0.01 mol) were dispersed in water–ethanol (1:10 V/V) and CH_3COOH was added as a catalyst. The mixture were stirred by mechanical stirring and refluxed at 85 °C for at least 24 h. Then the solvents were evaporated slowly at 100 °C under continuous stirring until the brown gel was formed. After being dried at 100 °C for 10 h, the power was fine grinded by ball-milling with sucrose and acetone at least for 8 h. After evaporating the acetone, the dry powder was calcinated in a horizontal quartz tube oven at 700 °C for 10 h at argon atmosphere to obtain the Li_2FeSiO_4/C composite.

2.3. Materials characterization

The structures of Fe_2O_3 and Li_2FeSiO_4/C composite were determined by X-ray diffraction (XRD, Rigaku, D/max-2200 PC) with Cu Kα radiation operated at 40 kV and 20 mA. The morphologies of Fe_2O_3 and Li_2FeSiO_4/C composite were observed by using a field-emission scanning electron microscope (FE-SEM, NOVA NanoSEM 230) and a high-resolution transmission electron microscope (HR-TEM, JEM-2010HT). The amount of carbon in Li_2FeSiO_4/C composite was 16 wt% measured by using a high frequency carbon–sulfur infrared analyzer (CSI, Shanghai Baoying Photoelectric Technology Co. Ltd., CS-206).

2.4. Electrode preparation and electrochemical measurements

The electrochemical performances of Li_2FeSiO_4/C composites were assessed using CR-2016 coin cells. The cathode was prepared by mixing 80 wt% of Li_2FeSiO_4/C composites with 10 wt% carbon black and 10 wt% poly(vinylidene fluoride) (PVDF) dissolved in *N*-methyl-2-pyrrolidine (NMP). All reported capacity values were quoted with respect to the mass of the Li_2FeSiO_4. The electrodes were formed by coating the slurry onto Al foils after drying overnight at 110 °C in a vacuum oven, and the typical cathode loading was 1–2 mg cm^{-2}. The cells were assembled with the cathode as prepared, with Li metal as the anode, and with glass fiber (Whatman GF/A) as the separator. The electrolytes were 1 M $LiPF_6$ dissolved in ethylene carbonate/dimethyl carbonate (1:1 w/w). Cell assembling was carried out in a glove-box (Braun, Master 100 Lab) full-filled with argon atmosphere. Galvanostatic charge–discharge measurements were executed between 1.5 and 4.8 V at room temperature by a Land CT 2001 battery test system, and 1 C rate was corresponding to current density of 160 mAh g^{-1}. Because of the sensitivity of the material in air, materials characterization and cells assembling were completed in a week after the materials preparation.

3. Results and discussions

The structures of iron oxide and Li_2FeSiO_4/C composite are determined by XRD. It can be easily found from Fig. 1a that the pattern is indexed to Fe_2O_3 (JCPDS 25-1402), which indicates that the Fe source applied on the experiment is Fe_2O_3. As shown in Fig. 1b, the diffraction peaks of Li_2FeSiO_4/C composite are in full accord with the Li_2FeSiO_4 structure indexed by orthorhombic $Pmn2_1$ [6,30,31]. The diffraction peaks of the carbon coating are not observed in the XRD pattern due to its amorphous state. It is interesting that no iron oxides, lithium silicates, and other impurities phases are observed for the resulting product. In previous reports, the reductive atmospheres were often used to suppress the formation of iron oxides impurities [6,9,24]. In our preparation,

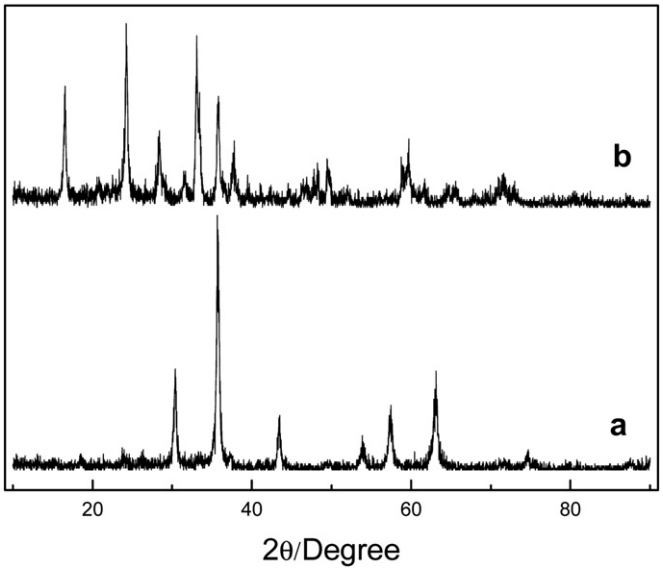

Fig. 1. XRD patterns of (a) Fe_2O_3 and (b) Li_2FeSiO_4/C.

carbon is the only reducer, which is generated from the carbonization of sucrose during the calcination process. It suggests that the Fe_2O_3 particles react with Li and Si sources under the reduction of carbon to produce the Li_2FeSiO_4 during the calcination process, and the presence of carbon has no effect on the development of Li_2FeSiO_4 phase. In a word, the result of XRD measurement indicates that the Li_2FeSiO_4/C composite prepared by sol–gel method with Fe_2O_3 shows the pure phase.

The morphologies of Fe_2O_3 and Li_2FeSiO_4/C composite are examined by FE-SEM and HR-TEM. Fig. 2a–d shows the SEM images of Fe_2O_3 and Li_2FeSiO_4/C composite. It can be seen in Fig. 2a that the Fe_2O_3 microspheres exhibit the regularly sphere shape with an average particle diameter of approximately 500 nm. According to the magnified SEM image shown in Fig. 2b, it is obvious that the microsphere is a result of an agglomeration of the smaller nanoparticles. To guarantee the homogeneity of dry gel, the monodisperse Fe_2O_3 microsphere is pursued in this preparation. Interestingly, as shown in the SEM images of Li_2FeSiO_4/C composite (Fig. 2c and d), some sphere-like particles with the bumped surface, which is attributed to the carbon coating probably, can be observed easily, and the average particle diameter is close to the Fe_2O_3 microsphere's. TEM measurement is used to further investigate the particle size of Li_2FeSiO_4/C composite and the carbon coating, and the images are shown in Fig. 3a–c. Some sphere-like particles of Li_2FeSiO_4/C composite can be found from Fig. 3a. According to the magnified TEM image shown in Fig. 3b, the Li_2FeSiO_4/C composite is also a result of an agglomeration of the nanoparticles with an average particle size of approximately 50 nm, which is similar to the SEM result of Fe_2O_3 (Fig. 2a and b). The HR-TEM image in Fig. 3c reveals that the Li_2FeSiO_4 nanocrystals are wrapped by the amorphous carbon coating with the thick of several nanometers, although the boundary of them is obscure. Generally, these results indicate that the Fe_2O_3 microsphere can be pursued as the template to prepare the Li_2FeSiO_4/C nanocomposite with the sphere-like morphology.

Galvanostatic charge–discharge measurements are carried out to assess the electrochemical performances of Li_2FeSiO_4/C nanocomposite cathode. Fig. 4 shows the charge–discharge profiles at 0.1 C rate for different cycles. It can be found that the 2nd charge plateau is obviously lower than the initial one, however its discharge plateau is similar to the initial one, which suggests that a Li/Fe disordering process might occur during first charge [32]. The Li_2FeSiO_4/C nanocomposite delivers an initial discharge capacity of about 140 mAh g^{-1}, and the discharge capacity increases gradually with the increasing cycle number. The charge–discharge profiles of 10th and 15th cycles almost overlap the 5th one, which implies that the crystal structure is stable and there is no major structural change occurred after 5 cycles [33].

To investigate the cycle performance of the Li_2FeSiO_4/C nanocomposite, it is tested for 100 cycles at different rates, and the results are shown in Fig. 5. For the performance cycled at 0.1 C rate, after the discharge capacity increases during the initial several cycles, it is stable at about 160 mAh g^{-1} until the 50th cycle, which is about 96% of the theoretical capacity extracted 1 mol of Li^+ per

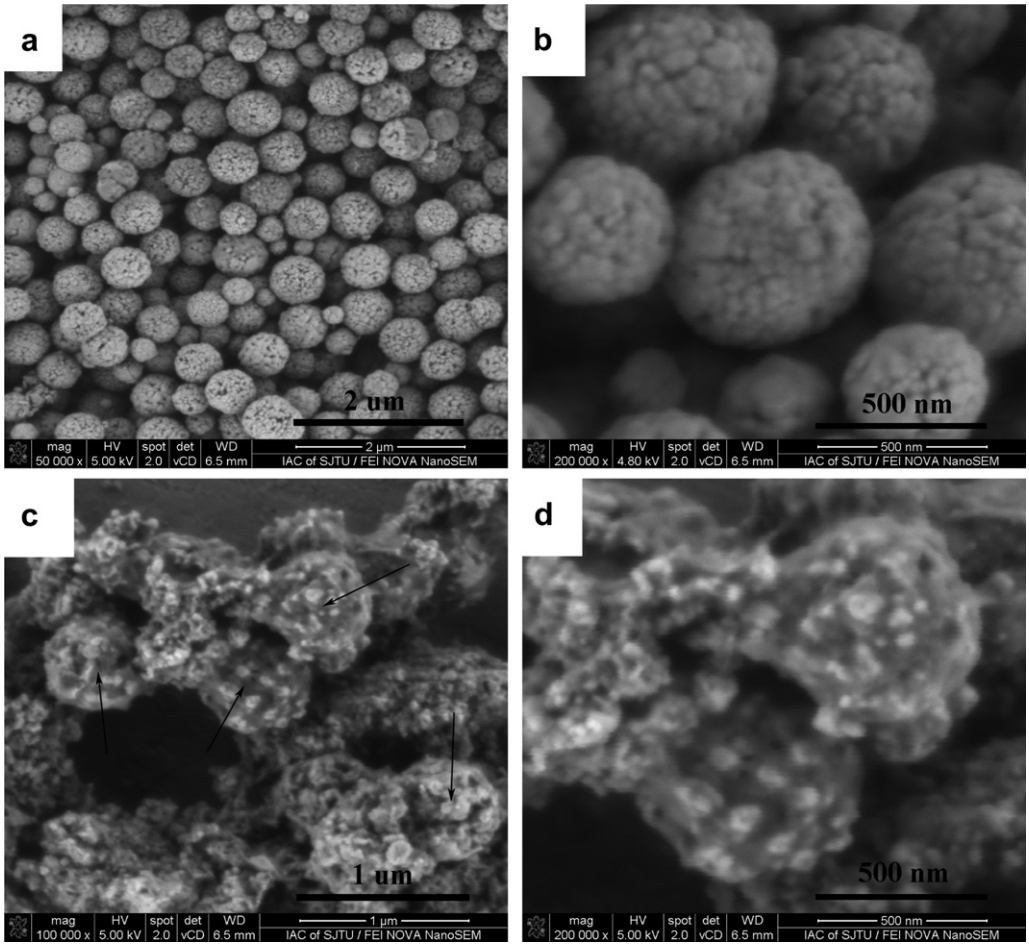

Fig. 2. SEM images of Fe_2O_3 microsphere at (a) low and (b) high magnification, and Li_2FeSiO_4/C nanocomposites at (c) low and (d) high magnification.

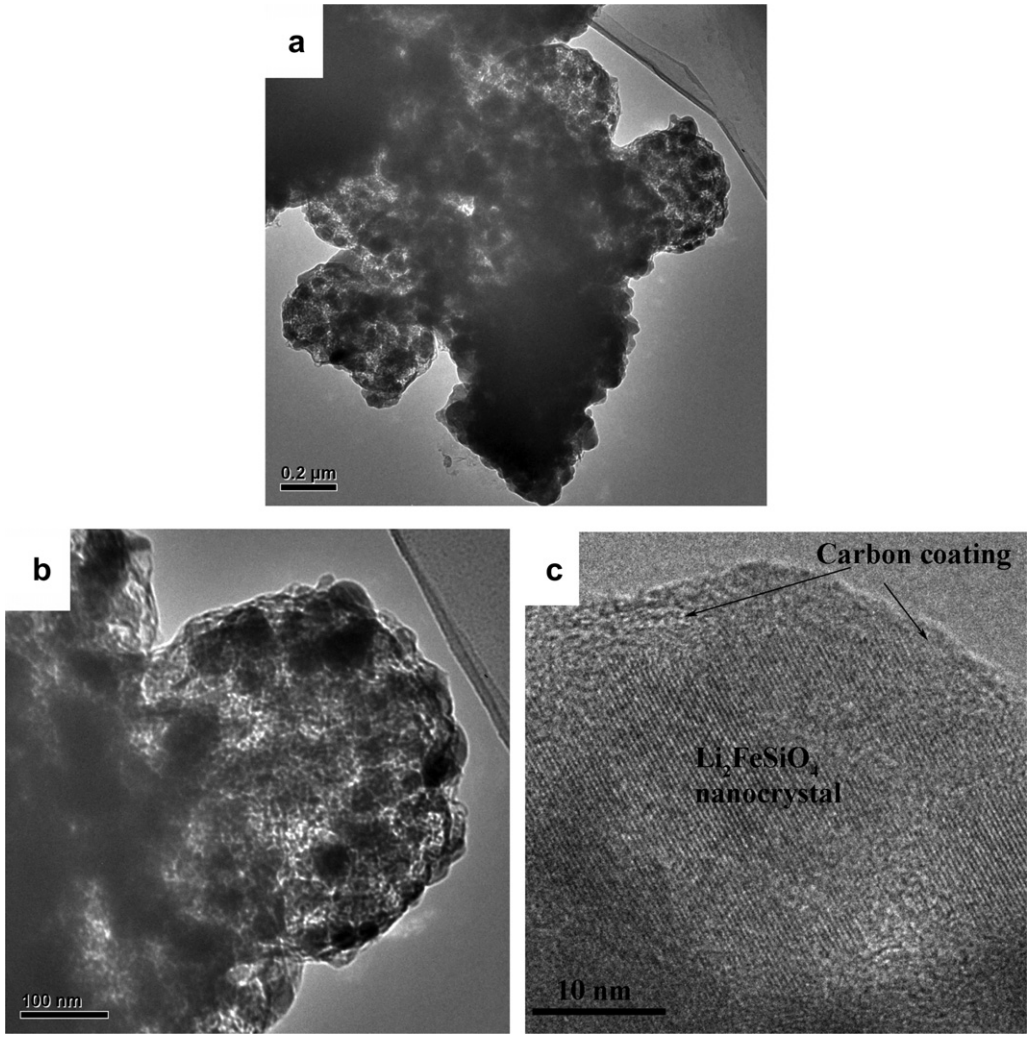

Fig. 3. TEM images of Li_2FeSiO_4/C nanocomposite at (a) low and (b) high magnification, and (c) HR-TEM image of Li_2FeSiO_4/C nanocomposite.

formula unit (166 mAh g^{-1}), then it slowly decreases with the increasing cycle number. Nevertheless, the discharge capacity is about 146 mAh g^{-1} in the 100th cycle, and about 91% of the maximum value is still retained. Apparently, the capacity decreases with the increasing of rate. For 0.2 C, 0.5 C, 1 C, and 2 C rate, the capacities also increase with the increasing cycle number during the initial some cycles, and they are stable at about 140 mAh g^{-1}, 115 mAh g^{-1}, 105 mAh g^{-1}, and 95 mAh g^{-1} until the 100th cycle,

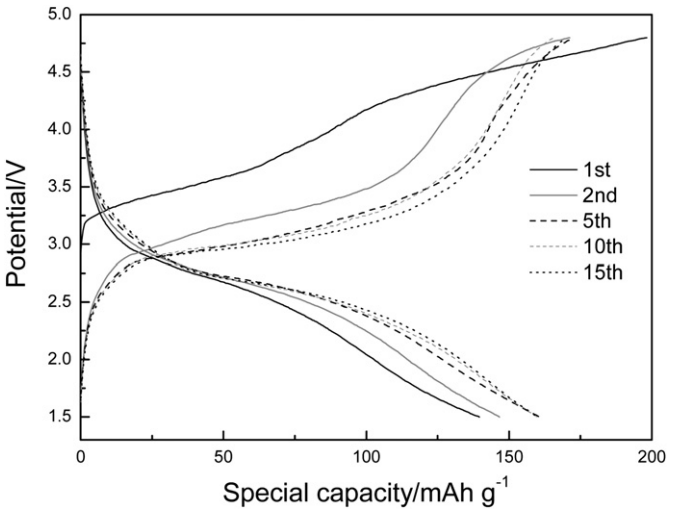

Fig. 4. Charge–discharge curves of Li_2FeSiO_4/C nanocomposite cycled at 0.1 C rate.

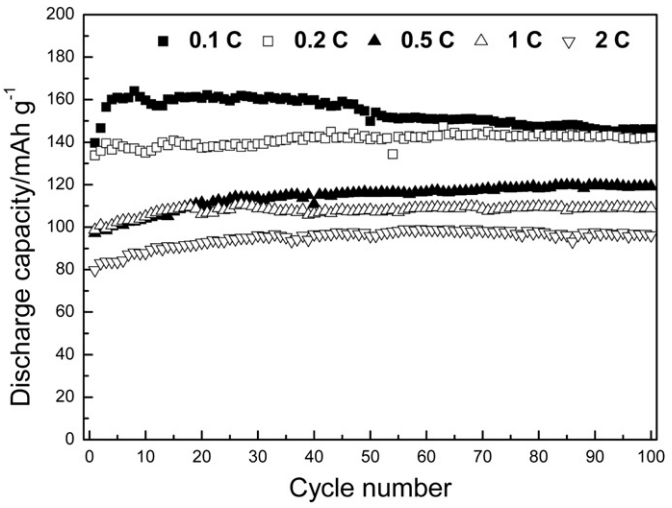

Fig. 5. The discharge capacities and cycle performances of Li_2FeSiO_4/C nanocomposite cycled at 0.1 C, 0.2 C, 0.5 C, 1 C, and 2 C rate.

respectively. Hitherto, in the potential range of 1.5–4.8 V, few researches about the cycle performance more than 50 times at 0.1 C or lower rate have been reported [12,19]. When the cell is tested at 0.1 C or lower rate, the charging process could be maintained for a long time in the high potential, where the side reactions between electrode and electrolyte are intensive. In order to obtain the stable cycle performance at the low rate in the wide potential range, the quality of carbon coating should be improved to restrain those side reactions. In this work, the Li_2FeSiO_4/C nanocomposite exhibits excellent cycle performance at different rates from 0.1 C to 2 C during 100 cycles, which implies that the carbon coating can prevent Li_2FeSiO_4 effectively from reacting with the PF_5 or HF from the $LiPF_6$ salt in the organic electrolyte [34]. The Li_2FeSiO_4/C nanocomposite has not exhibited higher capacity performance under the high-rate condition, and it could be attributed to its larger particle size of the active material. In the further investigation, we expect to synthesize Li_2FeSiO_4/C by using Fe_2O_3 with smaller particle size.

4. Conclusions

In summary, Li_2FeSiO_4/C nanocomposite has been synthesized as cathode material of lithium-ion battery by a template-assisted sol–gel method with Fe_2O_3 microsphere. It is found that the sample owns pure phase, sphere-like morphology, and nanostructure. The Li_2FeSiO_4/C exhibits stable cycle performance at different rates from 0.1 C to 2 C, and it delivers a high capacity of 160 mAh g^{-1} at 0.1 C rate in the 5th cycle and retains capacity of 146 mAh g^{-1} in the 100th cycle.

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